

PATENT ABSTRACTS OF JAPAN

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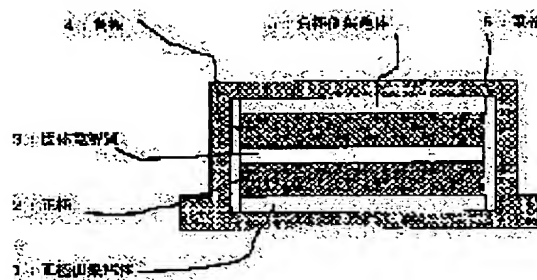
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(54) LITHIUM SECONDARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary cell of which particles of an activator and a solid state electrolyte are bonded with a bonding agent, having high ion conductivity and easy to manufacture.

SOLUTION: The lithium secondary cell composed of a lithium ion conductive solid state electrolyte arranged between a positive and a negative electrodes which are made of an activating material and enabled to occlude and release lithium ion reversibly, and particles of the activating material and the solid state electrolyte are bonded by macromolecule shown by the formula $(R_xSiO_y)_n$ [R: alkyl group or allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].



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CLAIMS

[Claim(s)]

[Claim 1]It is a lithium secondary battery which allocates a solid electrolyte which has lithium ion conductivity between an anode and a negative electrode which consist of an active material in which reversible occlusion discharge of a lithium ion is possible, A lithium secondary battery binding particles of said active material and a solid electrolyte with polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

[Claim 2]The aforementioned $(R_xSiO_y)_n$ [R : An alkyl group or an allyl group, The lithium secondary battery according to claim 1, wherein weight ratios contained in an electrode of polymers expressed with $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] or a solid electrolyte are 1 % of the weight - 15 % of the weight.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the lithium secondary battery which has improved the ion conductivity between the particles of an active material and a solid electrolyte especially about the lithium secondary battery used for mobile computing devices, such as a notebook computer and a cellular phone.

[0002]

[Description of the Prior Art]Conventionally, the organic electrolysis liquid which dissolved lithium salt in the organic solvent is used for the electrolyte of the lithium secondary battery used as a power supply of mobile computing devices.

The liquid spill had become a problem.

Then, many trials which use a solid electrolyte instead of organic electrolysis liquid have been made.

[0003]One of the solid electrolytes has a solid polymer electrolyte of the salt yne type in which polyether was made to dissolve lithium salt. In a salt yne type solid polymer electrolyte, when a lithium ion carries out hopping of between the oxygen atoms which are the elements (this element is hereafter called a hopping site.) which have a negative charge required for the ion conduction of a lithium ion, ion conduction becomes possible.

[0004]However, in a salt yne type solid polymer electrolyte, since the ion conduction of a counter ion occurred while the ion conduction of a lithium ion occurs, there was a problem that the transference number to lithium ion conduction became low.

[0005]On the other hand, as a solid electrolyte which only a lithium ion contributes to ion conduction, 0. Sulfide system noncrystalline solid electrolytes, such as $0.1\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M has an inorganic solid electrolyte like oxide stock crystalline substance solid electrolytes, such as trivalent positive ion], such as aluminum.

[0006]However, since an inorganic solid electrolyte was a brittle material, there was a problem that it was lacking in processability and slimming down was difficult.

[0007]Then, it is examined that it is compatible in high ionic conductivity and the outstanding processability by binding the particles of an inorganic solid electrolyte with insulating polymers. For example, in JP,63-78405,A, the solid electrolyte which bound the particles of the inorganic solid electrolyte with any one or more sorts of plastic materials chosen from the group of polyethylene, polypropylene, styrene butadiene rubber, neoprene rubber, and silicone rubber is proposed. With such a solid electrolyte, it should excel also in processability, with the high ionic conductivity of an inorganic solid electrolyte maintained.

[0008]

[Problem(s) to be Solved by the Invention]However, in the above solid electrolytes, since the particles of a solid electrolyte were bound with insulating polymers, when insulating polymers existed between the solid electrolyte and the electrode, there was a problem that an ion conduction course was intercepted. In order to avoid interception of an ion conduction course, in a JP,63-78405,A gazette. Thickness of the layer which consists of binding materials needed to be made into thickness almost equal to the particle diameter of the particles of a solid electrolyte, and there was a problem that it was difficult to manufacture the layer which consists of thickness of such one particle, without generating an inter-electrode short circuit.

[0009]This invention is made in view of the problem in the above-mentioned conventional technology, and the purpose is to provide the easy lithium secondary battery of manufacture, without reducing ion conductivity.

[0010]

[Means for Solving the Problem]A lithium secondary battery concerning claim 1 of this invention, It is a lithium secondary battery which allocates a solid electrolyte which has lithium ion conductivity between positive and negative poles which consist of an active material in which reversible occlusion discharge of a lithium ion is possible, Particles of said active material and a solid electrolyte were bound with polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

[0011]A lithium secondary battery concerning claim 2 of this invention, n [[aforementioned $(R_xSiO_y)_n$] R: It is the feature that weight ratios contained in an electrode of polymers expressed with an alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] or a solid electrolyte are 1 % of the weight - 15 % of the weight.

[0012]According to the lithium secondary battery of this invention, a $(R_xSiO_y)_n$ [R:alkyl group or an allyl group,

Since polymers expressed with $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] have a hopping site with high density, in such polymers existing near the point of contact of particles of an active material and a solid electrolyte. Even if it fills up with not a layer but two or more particles which can reduce resistance to ion conduction between particles, and consist of thickness of one particle like before by this in the direction of layer thickness, Since it becomes easy to manufacture without not intercepting the ion conduction course and as a result generating an inter-electrode short circuit, a lithium secondary battery used, for example as a power supply of mobile computing devices can be manufactured at a high rate of an excellent article.

[0013]

[Embodiment of the Invention]Hereafter, this invention is explained in detail based on a drawing. Drawing 1 is a sectional view showing the example of the lithium secondary battery of this invention. As for a solid electrolyte and 4, in drawing 1, the anode side charge collector and 2 are [the negative-electrode side charge collector and 6] battery cases a negative electrode, and 5 an anode and 3 1.

[0014]The anode 2 and the negative electrode 4 bind an active material with polymers. As an active material used for the anode 2 and the negative electrode 4, At least one kind in a spinel type lithium manganese multiple oxide, a spinel type lithium-nickel-manganese multiple oxide, a spinel type lithium titanium multiple oxide, a spinel type lithium niobium titanium multiple oxide, and a spinel type lithium iron titanium multiple oxide is used.

[0015]If there is no anisotropy, therefore which field of a crystal exists [these] in the point of contact between particles, in order that the channel of a lithium ion may take the three-dimensional structure, since it is uninfluential in the ejection and insertion of a lithium ion, they are active materials suitable for the lithium-secondary battery using a solid electrolyte. These active materials have a small volume change accompanying charge and discharge, therefore since the crystal collapse accompanying charge and discharge does not take place easily, they are active materials suitable for the lithium secondary battery using a solid electrolyte.

[0016]As polymers which bind the particles of positive active material and negative electrode active material, the polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$] are used.

[0017]Since the oxygen atom in which these polymers serve as a hopping site for lithium ion conduction exists with high density, when these polymers exist near the point of contact of particles, the resistance to the ion conduction between particles is reduced.

[0018]Such polymers are compounded from the monomer expressed with $RSi(OR)_3$ [R:alkyl group or allyl group] and $R_2Si(OR)_2$ [R:alkyl group or allyl group]. It is set to $x = 1$ and $y = 1.5$ when $RSi(OR)_3$ is 100%. If the addition of $R_2Si(OR)_2$ is increased, the increase of the flexibility of polymers and a binding property will become good, but since the number of hopping sites becomes fewer, ion conductivity falls. x is large, and y becomes small as the addition of $R_2Si(OR)_2$ is increased, but if set to $x > 1.4$ and $y < 1.3$, ion conductivity will fall extremely.

Therefore, the polymers of the range of $1 \leq x \leq 1.4$ and $1.3 \leq y \leq 1.5$ are used.

[0019>About $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$], in $n < 500$.

Shape maintenance of the solid electrolyte which bound the particles of the electrode which bound the particles of the active material, and the solid electrolyte is not enough, Since the solubility to solvents, such as toluene later mentioned in $n > 500,000$, becomes low, distribution with the particles of an active material and a solid electrolyte becomes uneven and contact of particles worsens, Since ionic conductivity falls or the usage fee of a solvent increases extremely to dissolve polymers thoroughly, it becomes difficult to deal with it.

[0020]As for the weight ratio contained further again in the electrode of the polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$], or a solid electrolyte, it is desirable that they are 1 % of the weight - 15 % of the weight.

[0021]In less than 1 % of the weight, since the density of a hopping site [/ near the point of contact of particles] is low and there are many openings, ionic conductivity falls. The above-mentioned polymers are what is added for the purpose of providing a hopping site near the point of contact of ion-conductive particles called the particles of an active material and a solid electrolyte. Since it will be the material which does not demonstrate ion conductivity in itself if there are no ion-conductive particles, if it exceeds 15 % of the weight, contact of particles will be checked and ionic conductivity will fall.

[0022]In order to produce the anode 2 or the negative electrode 4, a conducting agent, a $(R_xSiO_y)_n$ [R:alkyl group, or allyl groups, such as an active material and a charge of a conductive carbon material, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] are mixed, solvents, such as toluene, are added further, a slurry is adjusted, this slurry is applied to the anode side charge collector 1 or the negative-electrode side charge collector 5, and the method of hardening at 150-200 ** is used. Under the present circumstances, about 1% of the weight of an organotin compound may be added as a hardening accelerator. As such an organotin compound, dibutyldiacetoxytin etc. are used, for example.

[0023]The solid electrolyte 3 binds a lithium-ion-conductivity crystalline substance oxide with polymers, and as this lithium-ion-conductivity crystalline substance oxide, $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ [M aluminum or Ga], $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ [M aluminum or Ga], When a univalent or divalent positive ion and M of $Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$ [M are univalent and $n=1$ and M are divalent, as for $n=2$ and x, at least one kind in 0.1 - 0.5] is used.

[0024]The polymers same as polymers which bind the solid electrolyte 3 as the polymers which bind the particles of positive active material and negative electrode active material are used. That is, it is $(R_xSiO_y)_n$

[R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

[0025]In order to produce the solid electrolyte 3, $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$] is mixed with a lithium-ion-conductivity crystalline substance oxide, Furthermore solvents, such as toluene, are added, a slurry is adjusted, this slurry is applied to the anode 2 and/or the negative electrode 4, and the method of hardening at 150-200 ** is used.

[0026]Metallic foils, such as aluminium foil, are used for the anode side charge collector 1 and the negative-electrode side charge collector 5.

[0027]The laminate film which laminated a polyethylene terephthalate film, aluminium foil, a polyethylene film, etc. is used for the battery case 6.

[0028]

[Example]Next, an example is explained about the lithium secondary battery of this invention.

[0029][Example 1] $(R_xSiO_y)_n$ [R: (R_xSiO_y) Lithium secondary battery A of this invention was produced by binding the particles of an active material and a solid electrolyte using a methyl group, $x=1.2$, $y=1.4$, and $n=10,000-12,000$].

[0030] $Li_{1.1}Mn_{1.9}O_4$ which is positive active material 86 % of the weight, carrying out weighing of the $(R_xSiO_y)_n$ [R:methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] which are 9 % of the weight and a binder about acetylene black which is a conducting agent $(R_xSiO_y)_n$ 5% of the weight -- further -- toluene -- in addition, these were mixed and the slurry was adjusted.

[0031]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the anode was formed.

[0032] $Li_{1.33}Ti_{1.67}O_4$ which is negative electrode active material 88 % of the weight, carrying out weighing of the $(R_xSiO_y)_n$ [R:methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] which are 9 % of the weight and a binder about acetylene black which is a conducting agent $(R_xSiO_y)_n$ 3% of the weight -- further -- toluene -- in addition, these were mixed and the slurry was adjusted.

[0033]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the negative electrode was formed.

[0034] $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ which is a solid electrolyte 90 % of the weight, $(\text{R}_x\text{SiO}_y)_n$ [which is a binder (R_xSiO_y) -- R: -- carrying out weighing of a methyl group, $x=1.2$, $y=1.4$, and $n=10,000-12,000$] 10% of the weight -- further -- toluene -- in addition, these were mixed and the slurry was adjusted.

[0035] After applying this slurry to the anode and the negative electrode and pasting these together, it was made to harden by heat-treating at 200 °C for 2 hours, and the battery element was formed.

[0036] As for the size, the solid electrolyte set to 20 micrometers by the anode having set to 20 micrometers, and the negative electrode set 50x50 mm and thickness to 20 micrometers a total of 60 micrometers.

[0037] After carrying out vacuum drying of the battery element over 2 hours at 200 °C, it wrapped in the polyethylene terephthalate polyethylene aluminum polyethylene laminate film, and the battery case was formed by carrying out heating weld.

[0038] [Example 2] $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.4$, $y=1.3$, $n=10,000-12,000$] was used for the polymers used

for binding using the same active material material and solid electrolyte materials as Example 1, and lithium secondary battery B of this invention was produced. The weight ratio of a granular material and a binder and the manufacturing method were made the same as Example 1.

[0039] [Example 3] $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=200,000-250,000$] was used for the polymers used

for binding using the same active material material and solid electrolyte materials as Example 1, and lithium secondary battery C of this invention was produced. The weight ratio of a granular material and a binder and the manufacturing method were made the same as Example 1.

[0040] [Example 4] Using the same active material material and solid electrolyte materials as Example 1, $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=450,000-500,000$] was used for the polymers for binding, and lithium

secondary battery D of this invention was produced. The weight ratio of a granular material and a binder and the manufacturing method were made the same as Example 1.

[0041] [Example 5] The polymer material further used for binding is used using the same active material material and solid electrolyte materials as Example 1. About such composition ratios, it is an anode. -- $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] = 81/9/10 % of the weight,

Negative-electrode -- $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: A methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] = 86/9/5 % of the weight, Solid-electrolyte -- $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ / $(\text{R}_x\text{SiO}_y)_n$ [R: A methyl group, $x=1.2$, $y=1.4$, and lithium secondary battery E made into $n=10,000-12,000$] = 90 / 10 % of the weight were produced. Other manufacturing methods were made to be the same as that of Example 1.

[0042] [Example 6] Active material material, solid electrolyte materials, and the polymer material for binding are used like Example 1. About such composition ratios, it is an anode. -- $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] = 88/9/3 % of the weight, Negative-electrode -- $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: A methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] = 90/9/1 % of the weight, Solid-electrolyte -- $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ / $(\text{R}_x\text{SiO}_y)_n$ [R: A methyl group, $x=1.2$, $y=1.4$, and lithium secondary battery F made into $n=10,000-12,000$] = 90 / 10 % of the weight were produced. Other manufacturing methods were made to be the same as that of Example 1.

[Comparative example 1] $(\text{R}_x\text{SiO}_y)_n$ [R which separated from the polymers used for binding from the generic claim of this invention while using the same active material material and solid electrolyte materials as Example 1 : A methyl group, Lithium secondary battery G using $x=1.8$, $y=1.1$, and $n=10,000-12,000$] was produced. The weight ratio of a granular material and a binder and the manufacturing method were made to be the same as that of Example 1.

[Comparative example 2] Although the same active material material and solid electrolyte materials as Example 1 are used, $(\text{R}_x\text{SiO}_y)_n$ [R from which the molecular weight of the polymers used for binding separated from the generic claim of this invention: Lithium secondary battery H was produced using a methyl group, $x=1.2$, $y=1.4$, and $n=1,000,000-1,500,000$]. The weight ratio of a granular material and a binder and the manufacturing method were made to be the same as that of Example 1.

[Comparative example 3] Although the polymers for binding also use $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-$

12,000] which is a generic claim of this invention (R_xSiO_y) using the same active material material and solid electrolyte materials as Example 1, Such composition ratios are anodes. -- $Li_{1.1}Mn_{1.9}O_4$ / acetylene black / (R_xSiO_y)_n [R: methyl group, x= 1.2, y= 1.4, n=10,000-12,000]=71/9/20 % of the weight, Negative-electrode -- $Li_{1.33}Ti_{1.67}O_4$ / acetylene black / (R_xSiO_y)_n [R : A methyl group, x= 1.2, y= 1.4, n=10,000-12,000]=71/9/20 % of the weight, Solid electrolyte -- $Li_{1.3}aluminum_{0.3}Ti_{1.7}(PO_4)_3$ / (R_xSiO_y)_n [R : A methyl group, x= 1.2, y= 1.4, and n=10,000-12,000]=80 / 20 % of the weight, Lithium secondary battery I from which it separated from the generic claim of this invention was produced. Other manufacturing methods were made to be the same as that of Example 1.

[0043][Comparative example 4] While using the same active material material and solid electrolyte materials as Example 1, the polymers used for binding A (R_xSiO_y)_n [R: alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and not $500 \leq n \leq 500,000$] but the conventional lithium secondary battery J made into styrene butadiene rubber was produced. The weight ratio of a granular material and a binder and the manufacturing method were made to be the same as that of Example 1.

[0044] And when the charge-and-discharge capacitance characteristics of the positive-active-material standard were searched for with the current density of 100microA/cm² using the charge-and-discharge measuring device about these lithium secondary battery A, B, C, D, E, F, G, H, I, and J, the result as shown in Table 1 was obtained.

[0045]

[Table 1]

試料	正極活物質／負極活物質 充填量 (mg)	充電／放電容量 (mAh)
リチウム二次電池A	154 / 150	16 / 15
リチウム二次電池B	155 / 150	13 / 11
リチウム二次電池C	153 / 155	16 / 15
リチウム二次電池D	151 / 152	13 / 11
リチウム二次電池E	154 / 153	12 / 10
リチウム二次電池F	165 / 165	12 / 10
リチウム二次電池G	154 / 148	8 / 5
リチウム二次電池H	165 / 149	9 / 6
リチウム二次電池I	155 / 157	5 / 2
リチウム二次電池J	152 / 149	0 / 0

[0046] In this table, the fill ration (mg) of positive active material and negative electrode active material and the characteristic of charge-and-discharge capacity (mAh) are shown.

[0047] In the passage clear from the table, the lithium secondary batteries A-F concerning this invention show high charge-and-discharge capacity.

[0048] However, although it was polymers of the similar presentation, in lithium secondary battery G produced using the polymers which separate from the generic claim of this invention, charge-and-discharge capacity fell substantially. Charge-and-discharge capacity fell [the lithium secondary batteries H and I from which the weight ratio of a granular material and a binder separates from the generic claim of this invention] substantially. In conventional lithium secondary battery J bound using styrene butadiene rubber, charge-and-discharge capacity serves as zero.

[0049] The particles of the active material and solid electrolyte like this invention in this way A (R_xSiO_y)_n [R: alkyl group or an allyl group, In the lithium secondary battery bound with $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$], Since the polymers which bind particles have a hopping site with high density, it becomes a lithium secondary battery which can reduce the resistance to the ion conduction between particles, and, as a result, has good charge-and-discharge capacitance characteristics in such polymers existing near the point of contact of particles.

[0050] The particle diameter of the particles of a solid electrolyte was 0.5 micrometer, was having formed 20

micrometers and a thick solid electrolyte layer to this particle diameter, and in producing each sample of an above-mentioned example, it did not cause the short circuit between positive and negative poles.

[0051]

[Effect of the Invention]As mentioned above, in this invention, it used having bound the particles of the active material and the solid electrolyte with the polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group,

$1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

In the binder which has a hopping site with high density existing near the point of contact of the particles of an active material and a solid electrolyte by that cause, the lithium secondary battery which can reduce the resistance to the ion conduction between particles, and has a good battery characteristic as a result was able to be manufactured easily, and was able to be provided.

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TECHNICAL FIELD

[Field of the Invention]This invention relates to the manufacturing method of the lithium secondary battery which has improved the ion conductivity between the particles of an active material and a solid electrolyte especially about the lithium secondary battery used for mobile computing devices, such as a notebook computer and a cellular phone.

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PRIOR ART

[Description of the Prior Art]Conventionally, the organic electrolysis liquid which dissolved lithium salt in the organic solvent is used for the electrolyte of the lithium secondary battery used as a power supply of mobile computing devices.

The liquid spill had become a problem.

Then, many trials which use a solid electrolyte instead of organic electrolysis liquid have been made.

[0003]One of the solid electrolytes has a solid polymer electrolyte of the salt yne type in which polyether was made to dissolve lithium salt. In a salt yne type solid polymer electrolyte, when a lithium ion carries out hopping of between the oxygen atoms which are the elements (this element is hereafter called a hopping site.) which have a negative charge required for the ion conduction of a lithium ion, ion conduction becomes possible.

[0004]However, in a salt yne type solid polymer electrolyte, since the ion conduction of a counter ion occurred while the ion conduction of a lithium ion occurs, there was a problem that the transference number to lithium ion conduction became low.

[0005]On the other hand, as a solid electrolyte which only a lithium ion contributes to ion conduction, 0. Sulfide system noncrystalline solid electrolytes, such as $0.1\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M has an inorganic solid electrolyte like oxide stock crystalline substance solid electrolytes, such as trivalent positive ion], such as aluminum.

[0006]However, since an inorganic solid electrolyte was a brittle material, there was a problem that it was lacking in processability and slimming down was difficult.

[0007]Then, it is examined that it is compatible in high ionic conductivity and the outstanding processability by binding the particles of an inorganic solid electrolyte with insulating polymers. For example, in JP,63-78405,A, the solid electrolyte which bound the particles of the inorganic solid electrolyte with any one or more sorts of plastic materials chosen from the group of polyethylene, polypropylene, styrene butadiene rubber, neoprene rubber, and silicone rubber is proposed. With such a solid electrolyte, it should excel also in processability, with the high ionic conductivity of an inorganic solid electrolyte maintained.

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EFFECT OF THE INVENTION

[Effect of the Invention]As mentioned above, in this invention, it used having bound the particles of the active material and the solid electrolyte with the polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group,

$1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

In the binder which has a hopping site with high density existing near the point of contact of the particles of an active material and a solid electrolyte by that cause, the lithium secondary battery which can reduce the resistance to the ion conduction between particles, and has a good battery characteristic as a result was able to be manufactured easily, and was able to be provided.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, in the above solid electrolytes, since the particles of a solid electrolyte were bound with insulating polymers, when insulating polymers existed between the solid electrolyte and the electrode, there was a problem that an ion conduction course was intercepted. In order to avoid interception of an ion conduction course, in a JP,63-78405,A gazette. Thickness of the layer which consists of binding materials needed to be made into thickness almost equal to the particle diameter of the particles of a solid electrolyte, and there was a problem that it was difficult to manufacture the layer which consists of thickness of such one particle, without generating an inter-electrode short circuit.

[0009]This invention is made in view of the problem in the above-mentioned conventional technology, and the purpose is to provide the easy lithium secondary battery of manufacture, without reducing ion conductivity.

[Translation done.]

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MEANS

[Means for Solving the Problem]A lithium secondary battery concerning claim 1 of this invention, It is a lithium secondary battery which allocates a solid electrolyte which has lithium ion conductivity between positive and negative poles which consist of an active material in which reversible occlusion discharge of a lithium ion is possible, Particles of said active material and a solid electrolyte were bound with polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

[0011]A lithium secondary battery concerning claim 2 of this invention, n [[aforementioned (R_xSiO_y)] R: It is the feature that weight ratios contained in an electrode of polymers expressed with an alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] or a solid electrolyte are 1 % of the weight - 15 % of the weight.

[0012]According to the lithium secondary battery of this invention, a $(R_xSiO_y)_n$ [R:alkyl group or an allyl group,

Since polymers expressed with $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] have a hopping site with high density, in such polymers existing near the point of contact of particles of an active material and a solid electrolyte. Even if it fills up with not a layer but two or more particles which can reduce resistance to ion conduction between particles, and consist of thickness of one particle like before by this in the direction of layer thickness, Since it becomes easy to manufacture without not intercepting the ion conduction course and as a result generating an inter-electrode short circuit, a lithium secondary battery used, for example as a power supply of mobile computing devices can be manufactured at a high rate of an excellent article.

[0013]

[Embodiment of the Invention]Hereafter, this invention is explained in detail based on a drawing. Drawing 1 is a sectional view showing the example of the lithium secondary battery of this invention. As for a solid electrolyte and 4, in drawing 1, the anode side charge collector and 2 are [the negative-electrode side charge collector and 6] battery cases a negative electrode and 5 an anode and 3 1.

[0014]The anode 2 and the negative electrode 4 bind an active material with polymers. As an active material used for the anode 2 and the negative electrode 4, At least one kind in a spinel type lithium manganese multiple oxide, a spinel type lithium-nickel-manganese multiple oxide, a spinel type lithium titanium multiple oxide, a spinel type lithium niobium titanium multiple oxide, and a spinel type lithium iron titanium multiple oxide is used.

[0015]If there is no anisotropy, therefore which field of a crystal exists [these] in the point of contact between particles, in order that the channel of a lithium ion may take the three-dimensional structure, since it is uninfluential in the ejection and insertion of a lithium ion, they are active materials suitable for the lithium secondary battery using a solid electrolyte. These active materials have a small volume change accompanying charge and discharge, therefore since the crystal collapse accompanying charge and discharge does not take place easily, they are active materials suitable for the lithium secondary battery using a solid electrolyte.

[0016]As polymers which bind the particles of positive active material and negative electrode active material, the polymers expressed with $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$] are used.

[0017]Since the oxygen atom in which these polymers serve as a hopping site for lithium ion conduction exists with high density, when these polymers exist near the point of contact of particles, the resistance to the ion conduction between particles is reduced.

[0018]Such polymers are compounded from the monomer expressed with $RSi(OR)_3$ [R:alkyl group or allyl group] and $R_2Si(OR)_2$ [R:alkyl group or allyl group]. It is set to $x = 1$ and $y = 1.5$ when $RSi(OR)_3$ is 100%. If the addition

of $R_2Si(OR)_2$ is increased, the increase of the flexibility of polymers and a binding property will become good, but since the number of hopping sites becomes fewer, ion conductivity falls. x is large, and y becomes small as the addition of $R_2Si(OR)_2$ is increased, but if set to $x > 1.4$ and $y < 1.3$, ion conductivity will fall extremely.

Therefore, the polymers of the range of $1 \leq x \leq 1.4$ and $1.3 \leq y \leq 1.5$ are used.

[0019] About $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$], in $n < 500$.

Shape maintenance of the solid electrolyte which bound the particles of the electrode which bound the particles of the active material, and the solid electrolyte is not enough, Since the solubility to solvents, such as toluene later mentioned in $n > 500,000$, becomes low, distribution with the particles of an active material and a solid electrolyte becomes uneven and contact of particles worsens, Since ionic conductivity falls or the usage fee of a solvent increases extremely to dissolve polymers thoroughly, it becomes difficult to deal with it.

[0020] As for the weight ratio contained further again in the electrode of the polymers expressed with $(R_xSiO_y)_n$

[R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$], or a solid electrolyte, it is desirable that they are 1 % of the weight - 15 % of the weight.

[0021] In less than 1 % of the weight, since the density of a hopping site [/ near the point of contact of particles] is low and there are many openings, ionic conductivity falls. The above-mentioned polymers are what is added for the purpose of providing a hopping site near the point of contact of ion-conductive particles called the particles of an active material and a solid electrolyte, Since it will be the material which does not demonstrate ion conductivity in itself if there are no ion-conductive particles, if it exceeds 15 % of the weight, contact of particles will be checked and ionic conductivity will fall.

[0022] In order to produce the anode 2 or the negative electrode 4, a conducting agent, a $(R_xSiO_y)_n$ [R:alkyl group,

or allyl groups, such as an active material and a charge of a conductive carbon material, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$] are mixed, solvents, such as toluene, are added further, a slurry is adjusted, this slurry is applied to the anode side charge collector 1 or the negative-electrode side charge collector 5, and the method of hardening at 150-200 °C is used. Under the present circumstances, about 1% of the weight of an organotin compound may be added as a hardening accelerator. As such an organotin compound, dibutyldiacetoxytin etc. are used, for example.

[0023] The solid electrolyte 3 binds a lithium-ion-conductivity crystalline substance oxide with polymers, and as this lithium-ion-conductivity crystalline substance oxide, $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ [M aluminum or Ga], $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$ [M aluminum or Ga], When a univalent or divalent positive ion and M of $Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$ [M are univalent and $n=1$ and M are divalent, as for $n=2$ and x , at least one kind in 0.1 - 0.5] is used.

[0024] The polymers same as polymers which bind the solid electrolyte 3 as the polymers which bind the particles of positive active material and negative electrode active material are used. That is, it is $(R_xSiO_y)_n$

[R:alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$].

[0025] In order to produce the solid electrolyte 3, $(R_xSiO_y)_n$ [R:alkyl group or an allyl group, $1 \leq x \leq 1.4$,

$1.3 \leq y \leq 1.5$, $500 \leq n \leq 500,000$] is mixed with a lithium-ion-conductivity crystalline substance oxide, Furthermore solvents, such as toluene, are added, a slurry is adjusted, this slurry is applied to the anode 2 and/or the negative electrode 4, and the method of hardening at 150-200 °C is used.

[0026] Metallic foils, such as aluminium foil, are used for the anode side charge collector 1 and the negative-electrode side charge collector 5.

[0027] The laminate film which laminated a polyethylene terephthalate film, aluminium foil, a polyethylene film, etc. is used for the battery case 6.

[Translation done.]

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EXAMPLE

[Example]Next, an example is explained about the lithium secondary battery of this invention.

[0029][Example 1] $(R_xSiO_y)_n$ [R: (R_xSiO_y)] Lithium secondary battery A of this invention was produced by binding the particles of an active material and a solid electrolyte using a methyl group, $x=1.2$, $y=1.4$, and $n=10,000-12,000$.

[0030] $Li_{1.1}Mn_{1.9}O_4$ which is positive active material 86 % of the weight, carrying out weighing of the n [R:methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] which are 9 % of the weight and a binder about acetylene black which is a conducting agent (R_xSiO_y) 5% of the weight -- further -- toluene -- in addition, these were mixed and the slurry was adjusted.

[0031]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the anode was formed.

[0032] $Li_{1.33}Ti_{1.67}O_4$ which is negative electrode active material 88 % of the weight, carrying out weighing of the n [R:methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] which are 9 % of the weight and a binder about acetylene black which is a conducting agent (R_xSiO_y) 3% of the weight -- further -- toluene -- in addition, these were mixed and the slurry was adjusted.

[0033]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the negative electrode was formed.

[0034] $Li_{1.3}$ aluminum $_{0.3}Ti_{1.7}(PO_4)_3$ which is a solid electrolyte 90 % of the weight, n [which is a binder (R_xSiO_y) -- R: -- carrying out weighing of a methyl group, $x=1.2$, $y=1.4$, and $n=10,000-12,000$] 10% of the weight -- further -- toluene -- in addition, these were mixed and the slurry was adjusted.

[0035]After applying this slurry to the anode and the negative electrode and pasting these together, it was made to harden by heat-treating at 200 ** for 2 hours, and the battery element was formed.

[0036]As for the size, the solid electrolyte set to 20 micrometers by the anode having set to 20 micrometers, and the negative electrode set 50x50 mm and thickness to 20 micrometers a total of 60 micrometers.

[0037]After carrying out vacuum drying of the battery element over 2 hours at 200 **, it wrapped in the polyethylene terephthalate polyethylene aluminum polyethylene laminate film, and the battery case was formed by carrying out heating weld.

[0038][Example 2] $(R_xSiO_y)_n$ [R:methyl group, $x=1.4$, $y=1.3$, $n=10,000-12,000$] was used for the polymers used

for binding using the same active material material and solid electrolyte materials as Example 1, and lithium secondary battery B of this invention was produced. The weight ratio of a granular material and a binder and the manufacturing method were made the same as Example 1:

[0039][Example 3] $(R_xSiO_y)_n$ [R:methyl group, $x=1.2$, $y=1.4$, $n=200,000-250,000$] was used for the polymers used

for binding using the same active material material and solid electrolyte materials as Example 1, and lithium secondary battery C of this invention was produced. The weight ratio of a granular material and a binder and the manufacturing method were made the same as Example 1.

[0040][Example 4] Using the same active material material and solid electrolyte materials as Example 1, $(R_xSiO_y)_n$ [R:methyl group, $x=1.2$, $y=1.4$, $n=450,000-500,000$] was used for the polymers for binding, and lithium secondary battery D of this invention was produced. The weight ratio of a granular material and a binder and the manufacturing method were made the same as Example 1.

[0041][Example 5] The polymer material further used for binding is used using the same active material material and solid electrolyte materials as Example 1, About such composition ratios, it is an anode. -- $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$]=81/9/10 % of the weight, Negative-electrode -- $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R : A methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$]=86/9/5 % of the weight, Solid-electrolyte -- $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/(\text{R}_x\text{SiO}_y)_n$ [R: A methyl group, $x=1.2$, $y=1.4$, and lithium secondary battery E made into $n=10,000-12,000$]=90 / 10 % of the weight were produced. Other manufacturing methods were made to be the same as that of Example 1.

[0042][Example 6] Active material material, solid electrolyte materials, and the polymer material for binding are used like Example 1, About such composition ratios, it is an anode. -- $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$]=88/9/3 % of the weight, Negative-electrode -- $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R : A methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$]=90/9/1 % of the weight, Solid-electrolyte -- $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/(\text{R}_x\text{SiO}_y)_n$ [R: A methyl group, $x=1.2$, $y=1.4$, and lithium secondary battery F made into $n=10,000-12,000$]=90 / 10 % of the weight were produced. Other manufacturing methods were made to be the same as that of Example 1.

[Comparative example 1] $(\text{R}_x\text{SiO}_y)_n$ [R which separated from the polymers used for binding from the generic claim of this invention while using the same active material material and solid electrolyte materials as Example 1 : A methyl group, Lithium secondary battery G using $x=1.8$, $y=1.1$, and $n=10,000-12,000$] was produced. The weight ratio of a granular material and a binder and the manufacturing method were made to be the same as that of Example 1.

[Comparative example 2] Although the same active material material and solid electrolyte materials as Example 1 are used, $(\text{R}_x\text{SiO}_y)_n$ [R from which the molecular weight of the polymers used for binding separated from the generic claim of this invention: Lithium secondary battery H was produced using a methyl group, $x=1.2$, $y=1.4$, and $n=1,000,000-1,500,000$]. The weight ratio of a granular material and a binder and the manufacturing method were made to be the same as that of Example 1.

[Comparative example 3] Although the polymers for binding also use $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$] which is a generic claim of this invention $(\text{R}_x\text{SiO}_y)_n$ using the same active material material and solid electrolyte materials as Example 1, Such composition ratios are anodes. -- $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R: methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$]=71/9/20 % of the weight, Negative-electrode -- $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ / acetylene black / $(\text{R}_x\text{SiO}_y)_n$ [R : A methyl group, $x=1.2$, $y=1.4$, $n=10,000-12,000$]=71/9/20 % of the weight, Solid electrolyte -- $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/(\text{R}_x\text{SiO}_y)_n$ [R : A methyl group, $x=1.2$, $y=1.4$, and $n=10,000-12,000$]=80 / 20 % of the weight, Lithium secondary battery I from which it separated from the generic claim of this invention was produced. Other manufacturing methods were made to be the same as that of Example 1.

[0043][Comparative example 4] While using the same active material material and solid electrolyte materials as Example 1, the polymers used for binding A $(\text{R}_x\text{SiO}_y)_n$ [R: alkyl group or an allyl group, $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and not $500 \leq n \leq 500,000$] but the conventional lithium secondary battery J made into styrene butadiene rubber was produced. The weight ratio of a granular material and a binder and the manufacturing method were made to be the same as that of Example 1.

[0044] And when the charge-and-discharge capacitance characteristics of the positive-active-material standard were searched for with the current density of $100\text{microA}/\text{cm}^2$ using the charge-and-discharge measuring device about these lithium secondary battery A, B, C, D, E, F, G, H, I, and J, the result as shown in Table 1 was obtained.

[0045]

[Table 1]

試料	正極活物質／負極活物質 充填量 (mg)	充電／放電容量 (mAh)
リチウム二次電池A	154 / 150	16 / 15
リチウム二次電池B	155 / 150	13 / 11
リチウム二次電池C	153 / 155	16 / 15
リチウム二次電池D	151 / 152	13 / 11
リチウム二次電池E	154 / 153	12 / 10
リチウム二次電池F	155 / 155	12 / 10
リチウム二次電池G	154 / 148	8 / 5
リチウム二次電池H	155 / 149	9 / 6
リチウム二次電池I	155 / 157	5 / 2
リチウム二次電池J	152 / 149	0 / 0

[0046]In this table, the fill ration (mg) of positive active material and negative electrode active material and the characteristic of charge-and-discharge capacity (mAh) are shown.

[0047]In the passage clear from the table, the lithium secondary batteries A-F concerning this invention show high charge-and-discharge capacity.

[0048]However, although it was polymers of the similar presentation, in lithium secondary battery G produced using the polymers which separate from the generic claim of this invention, charge-and-discharge capacity fell substantially. Charge-and-discharge capacity fell [the lithium secondary batteries H and I from which the weight ratio of a granular material and a binder separates from the generic claim of this invention] substantially. In conventional lithium secondary battery J bound using styrene butadiene rubber, charge-and-discharge capacity serves as zero.

[0049]The particles of the active material and solid electrolyte like this invention in this way $A(R_xSiO_y)_n$ [R:alkyl group or an allyl group, In the lithium secondary battery bound with $1 \leq x \leq 1.4$, $1.3 \leq y \leq 1.5$, and $500 \leq n \leq 500,000$], Since the polymers which bind particles have a hopping site with high density, it becomes a lithium secondary battery which can reduce the resistance to the ion conduction between particles, and, as a result, has good charge-and-discharge capacitance characteristics in such polymers existing near the point of contact of particles.

[0050]The particle diameter of the particles of a solid electrolyte was 0.5 micrometer, was having formed 20 micrometers and a thick solid electrolyte layer to this particle diameter, and in producing each sample of an above-mentioned example, it did not cause the short circuit between positive and negative poles.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view showing an example of the embodiment of the lithium secondary battery of this invention.

[Description of Notations]

1: The anode side charge collector, 2:anode, 3:solid electrolyte, and 4:negative-electrode side and 5:negative-electrode side charge collector, 6 : battery case

[Translation done.]

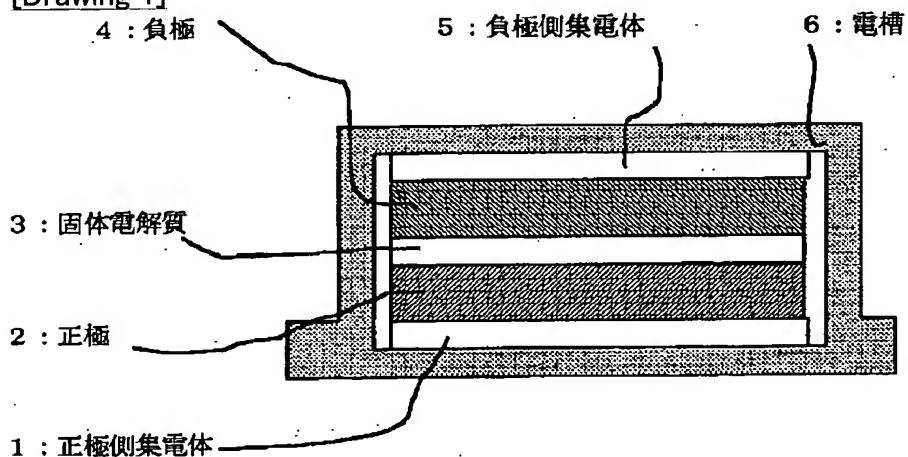
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DRAWINGS

[Drawing 1]



[Translation done.]

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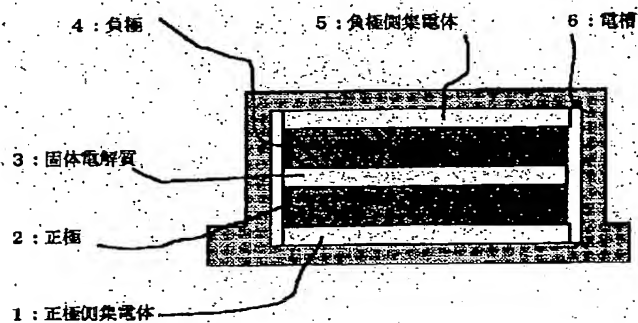
(54)【発明の名称】 リチウム二次電池

(57)【要約】

【課題】活物質および固体電解質の粒子を結着剤で結着したリチウム二次電池において、イオン伝導度が高い上に、製造の容易なリチウム二次電池を提供する。

【解決手段】リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間にリチウムイオン伝導性を有する固体電解質を配設してなるリチウム二次電池であって、上記活物質および固体電解質の粒子を、

(R, S i O_y)。[R:アルキル基またはアリル基、1 ≤ x ≤ 1.4、1.3 ≤ y ≤ 1.5、500 ≤ n ≤ 5000, 000] で表される高分子で結着する。



【特許請求の範囲】

【請求項1】リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間にリチウムイオン伝導性を有する固体電解質を配設してなるリチウム二次電池であって、前記活物質および固体電解質の粒子を、

$(R_xSiO_y)_n$ [R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 5000$ 、 000] で表される高分子で結着したことを特徴とするリチウム二次電池。

【請求項2】前記 $(R_xSiO_y)_n$ [R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 5000$ 、 000] で表される高分子の電極中または固体電解質中に含まれる重量比が、1重量%～15重量%であることを特徴とする請求項1に記載のリチウム二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はノートパソコンや携帯電話等のモバイル機器に使用されるリチウム二次電池に関し、特に活物質および固体電解質の粒子間のイオン伝導性を改善したリチウム二次電池の製造方法に関するものである。

【0002】

【従来の技術】従来、モバイル機器の電源として用いられるリチウム二次電池の電解質には、リチウム塩を有機溶媒に溶解した有機電解液が用いられており、漏液が問題となっていた。そこで、有機電解液の代わりに固体電解質を用いる試みが多数なされてきた。

【0003】固体電解質の一つに、ポリエーテルにリチウム塩を溶解させたソルトインタイプの高分子固体電解質がある。ソルトインタイプの高分子固体電解質では、リチウムイオンのイオン伝導に必要な負電荷を有する元素（以下、この元素をホッピングサイトと呼ぶ。）である酸素原子の間をリチウムイオンがホッピングすることによりイオン伝導が可能となる。

【0004】しかしながら、ソルトインタイプの高分子固体電解質では、リチウムイオンのイオン伝導があると同時に、対イオンのイオン伝導があるため、リチウムイオン伝導に対する輸率が低くなるという問題があった。

【0005】一方、リチウムイオンのみがイオン伝導に寄与する固体電解質として、 $0.01Li_3PO_4-0.63Li_2S-0.36SiS_2$ などの硫化物系非晶質固体電解質や、 $Li_{1-x}M_xTi_2(PO_4)_3$ [MはAlなどの3価の陽イオン]などの酸化物系結晶質固体電解質のような無機固体電解質がある。

【0006】しかしながら、無機固体電解質は脆性材料であるため、加工性に乏しく、薄型化が困難であるという問題があった。

【0007】そこで、絶縁性の高分子で無機固体電解質の粒子を結着することで、高いイオン伝導度と優れた加

工性を両立することが検討されている。例えば特開昭63-78405号公報では、ポリエチレン、ポリプロピレン、スチレンブタジエンゴム、ネオプレンゴム、シリコンゴムの群から選ばれるいずれか1種以上の可塑性材料で無機固体電解質の粒子を結着した固体電解質を提案している。このような固体電解質では、無機固体電解質の高いイオン伝導度を維持したまま、加工性にも優れたものとする事ができる。

【0008】

【発明が解決しようとする課題】しかしながら、上記のような固体電解質においては、固体電解質の粒子を絶縁性の高分子で結着しているため、固体電解質と電極との間に絶縁性の高分子が存在すると、イオン伝導経路が遮断されるという問題があった。イオン伝導経路の遮断を避けるため、特開昭63-78405号公報では、結着材からなる層の厚みを固体電解質の粒子の粒径とほぼ等しい厚さにする必要があり、このような粒子1個の厚さからなる層を、電極間の短絡を発生させずに製造することは難しいという問題点があった。

【0009】本発明は上記従来技術における問題点に鑑みてなされたものであり、その目的は、イオン伝導性を低下させることなく、製造の容易なりチウム二次電池を提供することにある。

【0010】

【課題を解決するための手段】本発明の請求項1に係るリチウム二次電池は、リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正負極間にリチウムイオン伝導性を有する固体電解質を配設してなるリチウム二次電池であって、前記活物質および固体電解質の粒子を、

$(R_xSiO_y)_n$ [R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 5000$ 、 000] で表される高分子で結着したことを特徴とするものである。

【0011】本発明の請求項2に係るリチウム二次電池は、前記 $(R_xSiO_y)_n$ [R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 5000000$] で表される高分子の電極中または固体電解質中に含まれる重量比が、1重量%～15重量%であることが特徴である。

【0012】本発明のリチウム二次電池によれば、 $(R_xSiO_y)_n$ [R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 5000$ 、 000] で表される高分子が、ホッピングサイトを高密度に有することから、このような高分子が活物質および固体電解質の粒子の接触点近傍に存在することで、粒子間のイオン伝導に対する抵抗を低減でき、これにより、従来のように粒子1個の厚さからなる層ではなく複数個の粒子が層の厚さ方向に充填されていても、そのイオン伝導経路が遮断されることがなく、その結果、電極間の短絡を発生させずに製造することが容易になるため、例

$n > 500,000$ では後述するトルエンなどの溶剤への溶解度が低くなり、活物質および固体電解質の粒子との分散が不均一になり、粒子同士の接触が悪くなるため、イオン伝導度が低下するか、あるいは高分子を完全に溶解するには溶剤の使用料が極端に増えるため、取り扱いにくくなる。

【0020】さらにまた、 $(R_xSiO_y)_n$ [R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 500,000$]で表される高分子の電極中または固体電解質中に含まれる重量比は1重量%~15重量%であることが望ましい。

【0021】1重量%未満では、粒子の接点近傍におけるホッピングサイトの密度が低く、空隙が多いため、イオン伝導度が低下する。また、上記高分子は、活物質および固体電解質の粒子といったイオン伝導性の粒子の接点近傍にホッピングサイトを提供することを目的として添加されるものであり、イオン伝導性の粒子がなければそれ自身はイオン伝導性を発揮しない材料であるため、15重量%を超えると、粒子同士の接触を阻害し、イオン伝導度が低下する。

【0022】正極2または負極4を作製するには、活物質と導電性炭素材料などの導電剤と ($R_xS_iO_y$)

n [R: アルキル基またはアリル基、 $1 \leq x \leq 1, 4$ 、 $1, 3 \leq y \leq 1, 5$ 、 $500 \leq n \leq 500, 000$] とを混合して、さらにトルエンなどの溶剤を加えてスラリーを調整し、このスラリーを正極側集電体 1 または負極側集電体 5 に塗布し、 $150 \sim 200^\circ\text{C}$ で硬化する方法が用いられる。この際、硬化促進剤として 1 重量% 程度の有機スズ化合物を添加してもよい。そのような有機スズ化合物としては、例えばジブチルジアセトキシスズなどが用いられる。

【0023】固体電解質3は、リチウムイオン伝導性結晶質酸化物を高分子で結着してなり、このリチウムイオン伝導性結晶質酸化物としては、 $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ [MはAlまたはGa]、 $\text{Li}_{1-(4-n)/5}\text{M}_n\text{Ti}_{2-n}\text{P}_3\text{O}_{12}$ [MはAlまたはGa]、 $\text{Li}_{1-(4-n)/5}\text{M}_n\text{Ti}_{2-n}\text{P}_3\text{O}_{12}$ [Mは1価または2価の陽イオン、Mが1価のとき $n=1$ 、Mが2価のとき $n=2$ 、 x は0.1~0.5]のうちの少なくとも1種類が用いられる。

【0024】固体電解質3を結着する高分子としては、正極活物質および負極活物質の粒子を結着する高分子と同じ高分子が用いられる。すなわち、 $(R_xSiO_y)_n$ 。

[R:アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 500,000$]である。

【0025】固体電解質3を作製するには、リチウムイオン伝導性結晶質酸化物と $(R, SiO_x)_n$ [R :アルキル基またはアリル基、 $1 \leq x \leq 1.4$ 、 $1.3 \leq y \leq 1.5$ 、 $500 \leq n \leq 500,000$]とを混合して、

さらにトルエンなどの溶剤を加えてスラリーを調整し、このスラリーを、正極2および/または負極4に塗布し、150~200℃で硬化する方法が用いられる。

【0026】正極側集電体1および負極側集電体5には、アルミニウム箔などの金属箔が用いられる。

【0027】電槽6には、ポリエチレンテレフタレートフィルム、アルミニウム箔、およびポリエチレンフィルムなどを積層したラミネートフィルムが用いられる。

【0028】

【実施例】次に本発明のリチウム二次電池について具体例を説明する。

【0029】〔実施例1〕 $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]を用いて、活物質および固体電解質の粒子を結着することにより、本発明のリチウム二次電池Aを作製した。

【0030】正極活物質である $Li_{1.1}Mn_{1.9}O_4$ を86重量%、導電剤であるアセチレンブラックを9重量%、結着剤である $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]を5重量%秤量し、さらにトルエンを加えて、これらを混合してスラリーを調整した。

【0031】このスラリーをアルミニウム箔上に塗布し、200℃で2時間熱処理することにより硬化させて正極を形成した。

【0032】負極活物質である $Li_{1.33}Ti_{1.67}O_4$ を88重量%、導電剤であるアセチレンブラックを9重量%、結着剤である $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]を3重量%秤量し、さらにトルエンを加えて、これらを混合してスラリーを調整した。

【0033】このスラリーをアルミニウム箔上に塗布し、200℃で2時間熱処理することによって硬化させて負極を形成した。

【0034】固体電解質である $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ を90重量%、結着剤である $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]を10重量%秤量し、さらにトルエンを加えて、これらを混合してスラリーを調整した。

【0035】このスラリーを正極および負極に塗布して、これらを張り合わせた後、200℃で2時間熱処理することによって硬化させて電池素子を形成した。

【0036】寸法は50×50mm、厚さは正極が20μm、固体電解質が20μm、負極が20μmの、計60μmとした。

【0037】電池素子を200℃で2時間かけて真空乾燥した後、ポリエチレンテレフタレート-ポリエチレン-アルミニウム-ポリエチレンラミネートフィルムで包んで、加熱融着することで電槽を形成した。

【0038】〔実施例2〕実施例1と同じ活物質材料と固体電解質材料を用い、結着のために用いる高分子に $(R_xSiO_y)_n$ [R:メチル基、 $x=1.4$ 、 $y=1.3$ 、 $n=10,000\sim12,000$]を用いて、本発明のリチウム二次電池Bを作製した。粉体と結着剤との重量比、および作製方法は実施例1と同じにした。

【0039】〔実施例3〕実施例1と同じ活物質材料と固体電解質材料を用い、結着のために用いる高分子に $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=200,000\sim250,000$]を用いて、本発明のリチウム二次電池Cを作製した。粉体と結着剤との重量比、および作製方法は実施例1と同じにした。

【0040】〔実施例4〕実施例1と同じ活物質材料と固体電解質材料を用い、結着用の高分子に $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=450,000\sim500,000$]を用いて、本発明のリチウム二次電池Dを作製した。粉体と結着剤との重量比、および作製方法は実施例1と同じにした。

【0041】〔実施例5〕実施例1と同じ活物質材料と固体電解質材料を用いて、さらに結着のために用いる高分子材料を用い、これらの組成比を、正極 $Li_{1.1}Mn_{1.9}O_4$ /アセチレンブラック/ $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=8.1/9/10重量%、負極 $Li_{1.33}Ti_{1.67}O_4$ /アセチレンブラック/ $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=86/9/5重量%、固体電解質 $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ / $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=90/10重量%としたリチウム二次電池Eを作製した。その他の作製方法は実施例1と同様にした。

【0042】〔実施例6〕実施例1と同じように、活物質材料、固体電解質材料、結着用の高分子材料を用い、これらの組成比を、正極 $Li_{1.1}Mn_{1.9}O_4$ /アセチレンブラック/ $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=88/9/3重量%、負極 $Li_{1.33}Ti_{1.67}O_4$ /アセチレンブラック/ $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=90/9/1重量%、固体電解質 $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ / $(R_xSiO_y)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=90/10重量%としたリチウム二次電池Fを作製した。その他の作製方法は実施例1と同様にした。

〔比較例1〕実施例1と同じ活物質材料と固体電解質材料を用いるとともに、結着のために用いる高分子を本発明の請求範囲から外れた $(R_xSiO_y)_n$ [R:メチル

基、 $x=1.8$ 、 $y=1.1$ 、 $n=10,000\sim12,000$ を用いたリチウム二次電池Gを作製した。粉体と結着剤との重量比、および、作製方法は実施例1と同様にした。

【比較例2】例1と同じ活物質材料と固体電解質材料を用いているが、結着のために用いる高分子の分子量が本発明の請求範囲から外れた $(R, SiO_x)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=1,000,000\sim1,500,000$]を用いて、リチウム二次電池Hを作製した。粉体と結着剤との重量比、および作製方法は実施例1と同様にした。

【比較例3】実施例1と同じ活物質材料と固体電解質材料を用い、結着用の高分子も本発明の請求範囲である $(R, SiO_x)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]を用いているが、これらの組成比が、正極 $Li_{1.1}Mn_{1.9}O_4$ /アセチレンブラック/ $(R, SiO_x)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=71/9/20重量%、負極 $Li_{1.33}Ti_{1.67}O_4$ /アセチレンブラック/ $(R, SiO_x)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=1$

*0,000~12,000]=71/9/20重量%、固体電解質 $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3/(R, SiO_x)_n$ [R:メチル基、 $x=1.2$ 、 $y=1.4$ 、 $n=10,000\sim12,000$]=80/20重量%と、本発明の請求範囲から外れたリチウム二次電池Iを作製した。その他の作製方法は実施例1と同様にした。

【0043】【比較例4】実施例1と同じ活物質材料と固体電解質材料を用いるとともに、結着のために用いる高分子を $(R, SiO_x)_n$ [R:アルキル基またはアリル基、 $1\leq x\leq 1.4$ 、 $1.3\leq y\leq 1.5$ 、 $500\leq n\leq 500,000$]ではなく、スチレンブタジエンゴムとした従来のリチウム二次電池Jを作製した。粉体と結着剤との重量比、および作製方法は例1と同様にした。

【0044】そして、これらリチウム二次電池A、B、C、D、E、F、G、H、I、およびJについて、充放電測定装置を用いて正極活物質基準の充放電容量特性を $100\mu A/cm^2$ の電流密度で求めたところ、表1に示すような結果が得られた。

【0045】

【表1】

試料	正極活物質/負極活物質 充填量 (mg)	充電/放電容量 (mAh)
リチウム二次電池A	154/150	16/15
リチウム二次電池B	155/150	13/11
リチウム二次電池C	153/155	16/15
リチウム二次電池D	151/152	13/11
リチウム二次電池E	154/153	12/10
リチウム二次電池F	155/155	12/10
リチウム二次電池G	154/148	8/5
リチウム二次電池H	155/149	9/6
リチウム二次電池I	155/157	5/2
リチウム二次電池J	152/149	0/0

【0046】この表においては、正極活物質および負極活物質の充填量 (mg) と、充放電容量 (mAh) の特性とを示す。

【0047】同表から明らかなとおり、本発明に係るリチウム二次電池A~Fが高い充放電容量を示している。

【0048】しかるに、類似の組成の高分子ではあるが、本発明の請求範囲から外れる高分子を用いて作製したリチウム二次電池Gにおいては、充放電容量が大幅に低下した。また、粉体と結着剤との重量比が本発明の請求範囲から外れるリチウム二次電池HおよびIも充放電容量が大幅に低下した。さらに、スチレンブタジエンゴムを用いて結着した従来のリチウム二次電池Jでは充放電容量がゼロとなっている。

【0049】かくして、本発明の如き、活物質および固体電解質の粒子を、 $(R, SiO_x)_n$ [R:アルキル基またはアリル基、 $1\leq x\leq 1.4$ 、 $1.3\leq y\leq 1.$

5、 $500\leq n\leq 500,000$]で結着したリチウム二次電池においては、粒子を結着する高分子がホッピングサイトを高密度に有することから、このような高分子が粒子の接点近傍に存在することで、粒子間のイオン伝導に対する抵抗を低減でき、その結果、良好な充放電容量特性を有するリチウム二次電池となる。

【0050】また、固体電解質の粒子の粒子径は $0.5\mu m$ であり、この粒子径に対して $20\mu m$ と厚い固体電解質層を形成したことで、上述の実施例の各サンプルを作製するに当たり、正負極間の短絡を起こすことがなかった。

【0051】

【発明の効果】以上のように、本発明によれば、活物質および固体電解質の粒子を、 $(R, SiO_x)_n$ [R:アルキル基またはアリル基、 $1\leq x\leq 1.4$ 、 $1.3\leq y\leq 1.5$ 、 $500\leq n\leq 500,000$]で表される高

分子で結着したことから、ホッピングサイトを高密度に有する結着剤が、活物質および固体電解質の粒子の接触点近傍に存在することで、粒子間のイオン伝導に対する抵抗を低減でき、その結果、良好な電池特性を有するリチウム二次電池を容易に製造し、提供することができた。

* 【図面の簡単な説明】

【図1】 本発明のリチウム二次電池の実施の形態の一例を示す断面図である。

【符号の説明】

1：正極側集電体、2：正極、3：固体電解質、4：負極、5：負極側集電体、6：電槽

【図1】

